[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

A Study of the Preparation and Quantitative Determination of Elementary Fluorine[1]

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A program of research now in progress in this Laboratory[2] deals with the action of fluorine upon organic compounds. Until recently, the element has been prepared by the electrolysis of molten potassium bifluoride, in an open generator of the Mathers type, and the fluorine produced has been regarded as fairly pure, in common with the views of others.[3] However, it was found that the gas was not completely absorbed by potassium iodide solution, the residue being largely oxygen; and also that it was partly condensable at the temperature of liquid air, which indicated that it contained a good deal of oxygen fluoride. The formation of these impurities was undoubtedly due to the presence of water in the molten electrolyte. The purpose of the present paper is to set forth the general conditions necessary for the production of pure fluorine, and to describe a generator embodying these principles, together with apparatus and methods for analyzing the product.

Apparatus and Methods

As the result of a rather careful survey of the literature,[4] we have considered, first, that fluorine must be generated free from oxygen and other impurities, rather than subjected to later purification; second, that the electrolysis of molten potassium bifluoride is the most promising and convenient method available for the purpose; and finally that the essential requirements for the formation of a pure product are an efficiently closed generator and an anhydrous electrolyte.

We have designed a new closed generator of the U-type, in contrast to the V-type described by Dennis, Veeder and Rochow.[5] It was constructed of heavy cast nickel and is illustrated in Fig. 1. It was strong, efficient and durable, as well as being suitable for pressure work. Nickel was chosen because it was resistant at operating temperatures, and formed a persistent, insoluble coating of nickel fluoride during the electrolysis. The apparatus was cast with flanged ends, and the caps were made by turning and drilling cast nickel forms. Lead washers were placed between the turned surfaces of the caps and the U-tube, and the connections made gas tight and rigid by drawing these parts together with heavy clamps, consisting of 13-mm. steel plates, provided with six 13-mm. steel bolts.

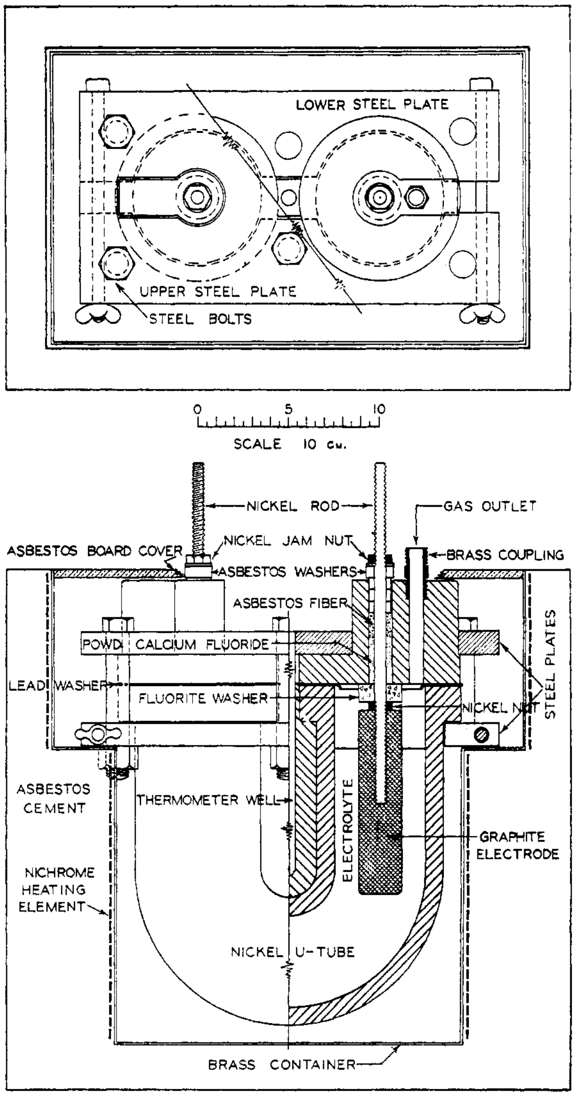

Fig. 1.—The fluorine generator.

Graphite electrodes were used, and threaded directly onto 6-mm. nickel rod supports. These, in turn, were centered in 13-mm. holes in the caps, and were held in place, made gas tight, and also insulated by means of a cement prepared from ground fluor spar and sodium silicate. Handles were made from 6-mm. iron rod, in the form of rectangles, which fitted under the ends of the steel clamp plates, and were folded and grasped together above the generator.

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[1] This paper is abstracted from the Doctorate thesis of William T. Miller, Jr., presented to the Graduate School of Arts and Sciences of Duke University in June, 1935.

[2] Previous papers, THIS JOURNAL, **55**, 4614 (1933); **56**, 2773 (1934).

[3] Simons, *ibid.*, **46**, 2175 (1924).

[4] The leading references describing the work upon which the following conclusions have been based are: (a) purification, Ruff and Menzel, *Z. anorg. Chem.*, **211**, 204 (1933); Ruff, *Z. angew. Chem.*, **46**, 739 (1933); (b) preparation, Ruff, "Die Chemie des Fluors," Julius Springer, Berlin, 1920; Lebeau and Damiens, *Compt. rend.*, **181**, 917 (1925); Ruff, *Z. angew. Chem.*, **47**, 480 (1934); (c) bifluoride melt hygroscopic, Fredenhagen and Krefft, *Z. Elektrochem.*, **35**, 671 (1929); Fredenhagen and Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

[5] Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

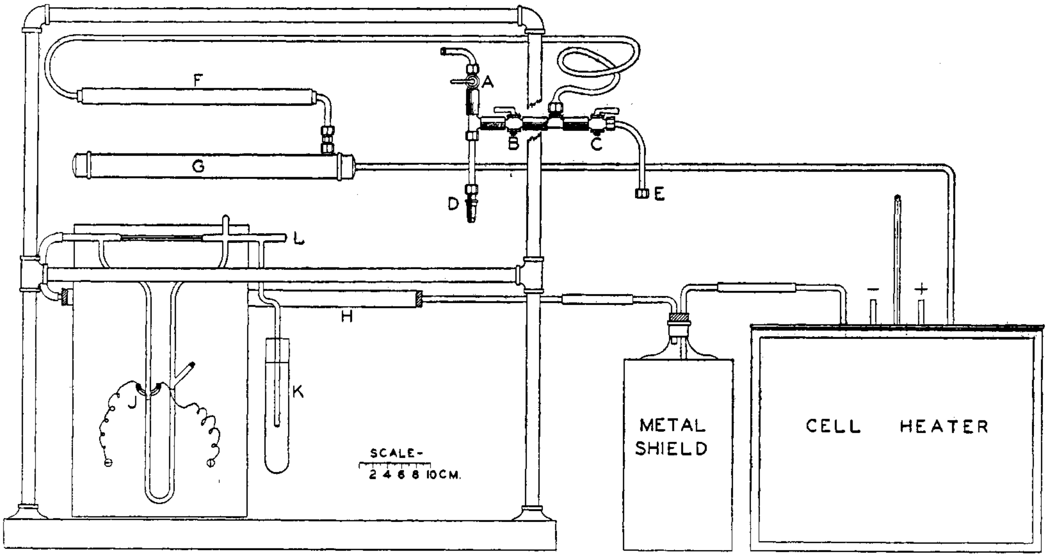

Fig. 2.—The apparatus assembly.

The construction of the heater is shown in Figs. 1 and 2. It consisted, essentially, of a brass container wound with a nichrome wire heating coil having resistance of 20.0 ohms. This unit was packed into an asbestos board box with dry asbestos cement hardened at the surface. The generator was placed in the heater in such a manner that the caps and couplings were kept sufficiently hot to fuse the low-melting sublimate from the electrolyte.

A special apparatus was designed to dehydrate the charge. It consisted essentially of a vertical copper pipe, approximately 48 × 8.3 cm., closed at the lower end, wound with nichrome wire (11.5 ohms), and insulated with asbestos cement. The top was closed by a cover, bolted on, using a lead washer, and carrying a copper exit tube and a thermometer well. From the bottom of the apparatus there extended a length of 13-mm. (i. d.) copper tubing, in the form of a spout, into the upper horizontal surface of which was soldered a 6-mm. brass coupling. In this apparatus, dry air, and finally fluorine gas, were passed through the salt, at an elevated temperature, entering from below. The salt was allowed to stand in contact with the fluorine for some time,[6] to complete the dehydration. Finally, by raising the temperature of the oven to 245° the salt was liquefied, and under these conditions ran down into the uninsulated spout, where it froze. With this arrangement, the dry electrolyte could be transferred very neatly to the generator by placing the latter, in its heater, and at about 260°, directly beneath the spout, and then melting the frozen salt with a Meker burner. The molten charge then flowed rapidly into the generator, which was immediately closed, thus ensuring a minimum exposure of the bifluoride to air and moisture in the process.

The set-up of apparatus which has been used for generating and handling the fluorine is illustrated in Fig. 2. The copper tubes G and H were filled with powdered sodium fluoride, which has been shown[5] to combine quantitatively with hydrogen fluoride. The tube F was filled with copper oxide wire, which, while not affected by the fluorine, would decompose quantitatively any ozone which might possibly be present. The container in the metal shield was a surge bottle in the hydrogen line, leading to a flow meter, which served also as an important safety device. It was arranged by means of a relay so as to sound an alarm whenever the flow of hydrogen was interrupted during the time that the apparatus was in operation. This avoided the danger of building up high pressures inside the generator by continuing the electrolysis with the exit tubes obstructed. However, by closing the hydrogen outlet L with a rubber cap and passing the gas through K, it was possible to apply any desired small pressure to the cathode chamber of the generator, in order to compensate for any such which might be built up in the anode compartment and the fluorine line.

The simplest, reasonably accurate analytical method for determining the efficiency of the generator consisted in allowing the fluorine produced in a measured time, at a definite current density, to react with a potassium iodide solution, and then to titrate the liberated iodine in the usual way. In the absence of oxygen fluoride, this method may be expected to give good results. No apparatus has been described in detail for carrying out this procedure, however, and the set-up which we have used is illustrated in Fig. 3. The U-tube was coated completely on the inside with a thin layer of ceresin wax, which was shown not to be attacked significantly by diluted fluorine (50% in air) at 0°. The rapid counter current flow of the solution produced by the screw pump promoted the complete absorption of the gas, without introducing any appreciable head of liquid. Gas samples, suitably diluted with air, were taken directly from the fluorine line through a slip joint, sealed with ceresin wax, at B. The 50-cc. bulb provided at C effectively prevented splashing, and the mercury seal made it possible to collect any unabsorbed gases quantitatively at A.

The precise determination of the fluorine contained in a gas sample, followed by the analysis of the residual gas,

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[6] Henglein and Stauf, U. S. Patent 1,914,425 (1933).

proved to be no simple problem. However, we have found experimentally that metallic mercury, when shaken, absorbed fluorine quantitatively. Also, we have observed that no significant absorption of the gas took place when it was stored for six hours at room temperature in a Pyrex glass bulb, and confined by means of mercury in a tube of small diameter. This was due to the perfect protective coating formed at the undisturbed surface of the metal, and to the fact that fluorine did not react with the glass under such conditions.

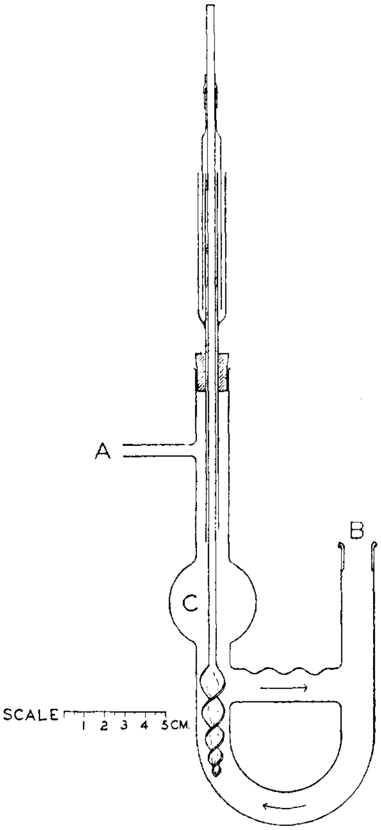

Fig. 3.—Absorption tube for the efficiency measurements.

Accordingly, a Pyrex glass buret, of the constant volume type, using mercury as the absorbent, has been designed, and is illustrated, with the jacket removed, in Fig. 4. Perhaps the most significant feature of this apparatus was the device for sealing in the fluorine sample with mercury at A and C. The arrangement at H and K served as a means of reference, so that manometer readings could be corrected for different positions of the buret, and also as a necessary bubble trap. The most satisfactory way to make clear the advantages and uses of the other connections shown is to describe at this point, in some detail, the method of collecting and measuring a sample of fluorine.

The buret was clamped in position, and the manometer attached at M, Fig. 4, using a little glycerol to prevent this connection from sticking. After lowering the level of the mercury in the manometer about 760 mm. below M, rubber caps were placed over tubes A, B and C, and the apparatus pumped out through J with an oil pump. Stopcocks D and G were both opened alternately in the two possible ways, in order to exhaust their bores as well as the rest of the apparatus, which was rinsed several times with dry air. Stopcock D was then closed and mercury admitted through G and its connecting tubes until the level of the liquid approximately reached F. After closing H and G the pump was shut off and the leveling bulb raised. The vacuum in the apparatus was then released through A or C, and the relative positions of K and F determined on the manometer scale by adjusting the mercury level to the respective marks, with H open. The tube B was filled about three-fourths full of mercury, which was freed from all adsorbed gases by gently warming and tapping the tube, which was exhausted at the same time from above. After again exhausting the apparatus, mercury was allowed to pass through D, in such a way as to fill the capillaries to the bottoms of both U-tubes as shown below C (Fig. 4). Similarly, E and the central tube leading up from F were filled with mercury, as shown in the figure, and the vacuum in the apparatus was then released with dry air. Before collecting the sample to be analyzed, the anode tube system from the generator was swept out for two hours, with a gas flow corresponding to a 5 amp. current. Then capillary C (Fig. 4) was slipped into the Monel metal fitting D (Fig. 2), the connection wrapped tightly with thin copper foil, and painted on the outside with ceresin wax. Fluorine was then passed through the pipet at the usual 5 amp. rate for one hour. The brass stopcock A (Fig. 2)

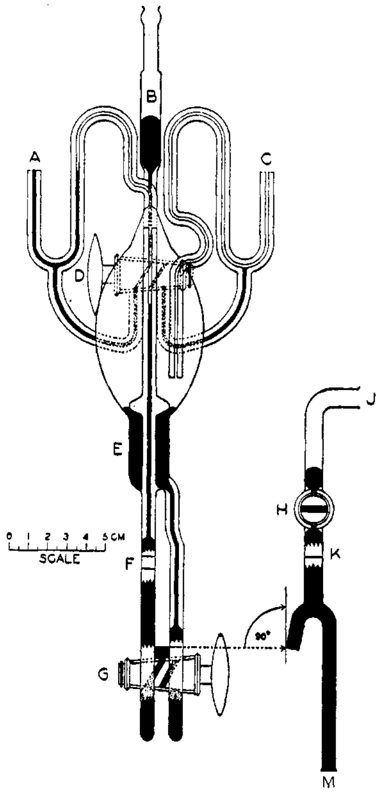

Fig. 4.—Gas buret for the quantitative estimation of fluorine.

was then opened, to by-pass the fluorine, and mercury allowed to fill the outlet U-tube of the absorption apparatus through D (Fig. 4), to the position shown at A in this figure. Then A was warmed with a small flame and a drop of sealing wax melted across the end of the tube and the mercury, taking care to exclude any air bubbles. After allowing the sample to stand in this way for five minutes, the brass stopcock B (Fig. 2) was closed, C opened, and the inlet U-tube likewise filled with mercury, disconnected at D (Fig. 2), and sealed. By passing heated air through the system in place of the generator gas, this method was shown experimentally to give a sample in the buret at the water-jacket temperature, and at atmospheric pressure, after the five-minute period of standing.

When the seals were completely hard, the buret was held in the hands, tilted to an angle of about 45°, with stopcock D leaning backward, and shaken so as to swirl the mercury in a thin film over the back portion of the bulb. A coating was formed at first, which quickly darkened as the fluorine reacted with it. The shaking was continued at short intervals, until this film remained bright for five minutes. The end-point was sharp, and signified the complete absorption of the fluorine. The pressure was then read at F, and the value thus obtained correlated with the atmospheric reading by correcting it to the corresponding position of K (Fig. 4) on the manometer scale.

To remove the residual gas from the pipet, mercury was admitted through G, until the pressure inside the bulb was approximately atmospheric. Then the tube B was connected by means of a section of 1-mm. capillary tubing, to a gas analysis apparatus similar to that described by Ambler.[7] The air was displaced from the tube by passing mercury out through the inlet capillary of the absorption apparatus through D and B. The residual gas was finally led out through the outlet capillary, also through D and B, into the Ambler apparatus, and analyzed in the usual way for carbon dioxide, oxygen and inert constituents.

Discussion of the Results

The new generator, set up and connected as described above, gave excellent results. It was easy to charge, quiet and steady in operation, and gave a closely reproducible product. The unit stood up very satisfactorily in service, being hardly at all corroded after five hundred hours of operation. The current efficiency measurements obtained showed a variation from 89–61%, falling off somewhat with time of electrolysis. The current was measured to 0.5%, the titration to about 0.2% and the time to about 0.3%, making a total of 1%. The error due to pressure changes was negligible. However, it should be noted that when the fluorine from the generator was passed into concentrated neutral potassium iodide solution, some hydrogen ion was formed, presumably due to the direct action of the halogen on the water, and to the extent of about 3% of the oxidizing value of the sample, under our operating conditions. According to Cady[8] when fluorine reacted with cold neutral water, oxidizing agents capable of liberating iodine were formed to the extent of 70% of the halogen absorbed. From this it was indicated that in our work the loss in oxidizing value from this cause should not exceed $0.30 \times 3 =$ approximately 1%. Consequently, the maximum total error in the efficiency measurements was considered to be not over 2.5%.

The purity of the fluorine generated, as measured by means of the mercury absorption buret described above, varied from 94 to 99% by volume, according to the age of the charge, and its initial moisture content. When the potassium bifluoride was finally dried with fluorine gas, the quality of the product was improved significantly. The best sample measured, prepared from an electrolyte which had been dried in this way, contained 99% fluorine, 0.4% oxygen, 0.2% carbon dioxide plus carbon oxyfluoride, and 0.4% inert gas, presumably carbon fluorides. The end-point of the absorption was sharp, as indicated by the appearance of the mercury. The principal experimental error of this method occurred in making the pressure readings, each of which could be observed to within ±0.2 mm., leading to a possible maximum error of 0.8 mm. This could affect the fluorine value by about ±0.15%, although it was more than likely that the errors would be at least partially compensating. Any variations due to temperature or pressure at the time of sampling, or volume changes due to the formation of mercury fluoride in the buret, have been shown to be entirely negligible. The values obtained for the composition of the residual gas were probably quite accurate, in terms of the total sample, because of the comparatively small portion of the latter which they represented. It should be pointed out, of course, that serious errors in all of these values would have resulted if the gas had contained any significant amounts of oxygen fluoride, which reacted slowly with mercury, with the evolution of oxygen.

From all of these considerations, it was clear that the closed generator described above was dependable, convenient, and yielded a closely reproducible product of a proven high degree of purity.

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[7] Ambler, *Analyst*, **54**, 517 (1929).

[8] Cady, This Journal, **57**, 246 (1935).

Experimental Part

The Preparation of Fluorine.—One kilogram of Merck purified potassium bifluoride, free from chloride and sulfate, was placed in the drying oven already described, and the lower opening of the spout closed with a rubber stopper. Then a current of dry air at reduced pressure was drawn through the salt at 150°, and at a rate of about 1.5 liters per hour, for twenty-four hours. After this, fluorine gas was passed into the oven from below until it issued from the top, and the salt allowed to stand in contact with the halogen for twelve hours at 150°. This treatment was repeated twice more with fresh fluorine. Then the bifluoride was melted in the oven by heating it to 245°, and transferred to the generator in the manner already described.

A preliminary electrolysis for one hour at 3 amp., and one-half hour at 5 amp. was carried out, in order to form a good insulating coating on the inside of the U-tube, and after this the generator was connected with the system shown in Fig. 2. It would then produce fluorine smoothly, either continuously or otherwise, for about 125 ampere-hours. Under normal operating conditions at 250°, a current of 5 amperes corresponded to a potential drop across the generator of 18–20 volts, and to a gas flow of approximately 2 liters per hour. In operating the unit, the safety alarm already mentioned was used always, and care taken to avoid any pressure changes which might force the molten electrolyte into either of the outlet tubes. Also between runs, the apparatus was maintained at 175°. It should be noted, in addition, that according to Fredenhagen and Cadenbach[4c] the exhausted electrolyte may be regenerated by treating it with anhydrous hydrogen fluoride, which was readily absorbed by the salt. However, we have not employed this technique up to the present time.

Current Efficiency of the New Generator.—The system was swept out with fluorine by operating the generator for one hour at 5 amp., with A and B closed, C open and E connected to a glass tube extending just under the surface of concentrated sulfuric acid. Meanwhile, the absorption apparatus was charged with 34 cc. of a 50% solution of potassium iodide in water, and attached to the system at D, by means of a metal sleeve, painted on the outside with ceresin wax. It was then surrounded by a small ice-bath, and rigidly clamped to avoid vibration. A right-angled glass tube was connected at A (Fig. 3), and arranged to lead the outlet gases through a little potassium iodide solution, in order to test the completeness of the absorption, although this was always practically quantitative. The stirrer was started at high speed, A (Fig. 2) was opened, and a slow current of air drawn in by applying a slight suction to the supplementary trap, in such a way that the generator gas would be diluted with about twice its volume of air. To do this the system was kept under a pressure of approximately 1–1.5 mm. of mercury less than atmospheric. Then the current was adjusted to a flow of precisely 5.00 amp., the exact time noted and the two stopcocks B and C turned simultaneously, the one on and the other off. The absorption was run for exactly fifteen minutes and was discontinued by again turning B and C simultaneously. The solution was finally washed out of the apparatus and an aliquot portion titrated with sodium thiosulfate in the usual way. The results obtained have been summarized in Table I.

TABLE I

THE CURRENT EFFICIENCY OF THE NEW GENERATOR *vs.* THE TIME OF THE ELECTROLYSIS

No.	Time of electrolysis to start of measurement Hrs.	Min.	Time interval between measurements Hrs.	Min.	Temp. of the electrolyte, °C.	Current eff., %
A-1	1	57	..	..	250	87.1
B-1	1	0	..	..	238	82.1
B-2	8	0	7	0	251	68.5
B-3	15	15	7	15	250	65.2
B-4	20	0	4	45	252	63.5
C-1	2	35	..	..	249	89.3
C-2	8	40	6	5	249	74.8
C-3	19	25	10	45	260	75.5
C-4	23	37	4	12	263	61.4

Analysis of the Gas Produced by the New Generator.—The system was set up as outlined above, and the mercury absorption buret attached at D (Fig. 2). The manipulation has already been described in detail, and the results obtained, including the analyses of the residual gas, are summarized in Table II.

TABLE II

COMPOSITION OF THE GAS PRODUCED BY THE NEW GENERATOR *vs.* THE TIME OF ELECTROLYSIS

No.	Time of electrolysis before sampling Hrs.	Min.	Temp., of electrolyte, °C.	% by volume of F_2	CO_2	O_2	Inert
A-1	11	30	265	95.4	1.1	2.2	1.3
B-1	16	30	250	94.8	0.71	3.7	0.79
C-1	25	0	260	94.4	0.63	2.8	2.17
D-1	7	55	249	97.1	0.97	1.6	0.43
D-2	18	50	256	98.8	..	..	..
E-1	8	25	251	97.4	1.3	0.98	0.32
F-1	3	30	247	96.5	1.8	1.4	.30
F-2	23	20	257	99.0	0.22	0.38	.40

The procedure for drying the charge with fluorine was introduced just before making run D-1, and the resulting improvement is clearly obvious.

Summary

1. A generator suitable for producing pure fluorine has been described. It consists of a heavy nickel U-tube, tightly closed to the air, and proved to be very efficient.

2. A novel apparatus for the quantitative determination of fluorine by absorption in metallic mercury has been designed. This has made possible a precise estimation of the constituents of the gas produced by the new generator.

3. A detailed procedure for the preparation of fluorine of known purity has been described for the first time. The product was found to contain 94–99% of the halogen.

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